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A review of the effects of catalyst and additive on biodiesel production, performance, combustion and emission characteristics

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ABSTRACT

This article is a literature review of the effect of different catalysts and additives on biodiesel production, performance, combustion and emission characteristics. This study is based on the reports of about 60 scientists who published their findings between 1998 and 2010. It was reported that base catalyst produced more biodiesel compared to acid type catalysts. There was not much variation in engine performance with the use of catalyst. Combustion characteristics were improved with the use of additives. It was found that ignition delay was reduced and premixed combustion duration was increased with the addition of catalyst. HC emission and PM emission were reduced with the use of catalysts.

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1. Introduction

Biodiesel is a renewable and environmental friendly alternative diesel fuel for diesel engine. Biodiesel is an oxygenated fuel which contains 10–15% oxygen by weight. Also it can be said a sulfur-free fuel. These facts lead biodiesel to complete combustion and less exhaust emissions than diesel fuel. Furthermore biodiesel has higher viscosity, density, pour point, flash point and cetane number than diesel fuel. Also the energy content or net calorific value of biodiesel is about 12% less than that of diesel fuel on a mass basis. Using biodiesel can help reduce the world's dependence on fossil fuels, and it also has significant environmental benefits. For example using biodiesel instead of the conventional diesel fuel significantly reduces the exhaust emissions such as the overall life circle of carbon dioxide (CO_2), particulate matter (PM), carbon monoxide (CO), sulfur oxides (SO_x), volatile organic compounds (VOCs), and unburned hydrocarbons (HC). Moreover biodiesel emits lower tail pipe exhaust emissions compared to the diesel fuel: nearly 50% less in PM emission, nearly 50% less in CO emission and about 68% less in HC emission. Furthermore, since biodiesel is a sulfur-free fuel, it has 99% less SO_x emission than the diesel fuel. Most of the biodiesels produce 10–15% higher oxides of nitrogen (NO_x) when fueling with 100% biodiesel. Depending on the abundant availability of feedstock in the local region, the different feedstocks are focused for the biodiesel production.

The use of catalyst/additive affects the biodiesel production, performance, combustion, and emission characteristics. This catalyst splits the oil into glycerine and biodiesel. Most of the biodiesel produced today is done with the base catalyzed reaction. The catalyst is typically sodium hydroxide or potassium hydroxide, which is dissolved in methyl alcohol. The reaction mix of oil and catalyst is kept just above the boiling point of the alcohol to speed up the reaction. Recommended reaction time varies between 1 and 8 h. Excess alcohol is normally used to ensure total conversion of the fat or oil to its esters. After separation of the glycerol and biodiesel phases, the excess alcohol is removed through the evaporation process or by distillation.

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2. Effect of catalyst on biodiesel production

Researchers and scientists have used different catalysts for biodiesel production from different bio fuels. A brief review of the effect of these catalysts is presented here. Most of the researchers/scientists have reported that the production of biodiesel is higher when a catalyst is used.

Transesterification of soybean oil with methanol was carried out at 60, 120, and 150 °C in the presence of a series NaX faujasite zeolite, ETS-10 zeolite, and metal catalysts by Galen J. Suppes et al. [1]. The stock zeolites were exchanged with potassium and cesium; NaX containing occluded sodium oxide (NaO_x/NaX) and occluded sodium azide (NaO_x/NaX*). The catalysts were calcined at 500 °C prior to use in order to increase activity. The ETS-10 catalysts provided higher conversions than the Zeolite-X type catalysts. Esterification of palmitic acid with methanol was studied by Sridarala Ramu et al. [2] on zirconia supported tungsten oxide solid acid catalysts prepared by both impregnation and co-precipitation methods. Dora E. López et al. [3] investigated the kinetics and selectivities of different solid catalysts for the transesterification of triacetin (a model compound for larger triglycerides as found in vegetable oils and fats) with methanol. Reaction was carried out at 60 °C in a batch reactor with a variety of solid and liquid, acid and base catalysts. The homogeneous phase (i.e., liquid) catalysts (NaOH and H_2SO_4) were studied for comparison. The deactivation characteristics of some of these catalysts were also studied. An environmentally benign process for the transesterification of soybean oil to methyl esters using alumina loaded with potassium as a solid base catalyst in a heterogeneous manner was developed by Wenlei Xie et al. [4]. The effects of various reaction variables such as the catalyst loading, oil to methanol ratio, reaction time and temperature on the conversion of soybean oil were investigated. Jaturong Jitputti et al. [5] reported on the preliminary results of using several acidic and basic solids, such as ZrO_2, ZnO, $SO_4{}^{2-}/SnO_2$, $SO_4{}^{2-}/ZrO_2$, KNO_3/KL zeolite and KNO_3/ZrO_2 as heterogeneous catalysts for crude palm kernel oil (PKO) and crude coconut oil (CCO) transesterification with methanol. It was found that ZnO and $SO_4{}^{2-}/ZrO_2$ exhibited the highest activity for both PKO and CCO transesterification.

An environmentally benign process for the methanolysis of soybean oil to methyl esters using calcined Mg–Al hydrotalcites as solid base catalysts in a heterogeneous manner was developed by Wenlei Xie et al. [6]. When the reaction was carried out at reflux of methanol, with a molar ratio of soybean oil to methanol of 15:1, a reaction time 9 h and a catalyst amount 7.5%, the oil conversion was 67%. The calcined hydrotalcite with an Mg/Al ratio of 3.0 derived from calcination at 773 K was found to be the optimum catalyst that could give the highest basicity and the best catalytic activity for this reaction. A novel application of Fe–Zn double-metal cyanide (DMC) complexes as solid catalysts in the preparation of fatty acid alkyl esters (biodiesel/biolubricants) from vegetable oils was reported by P.S. Sreeprasanth et al. [7]. Unlike the homogeneous or other solid catalysts (like ZnO–Al_2O_3, for example), the Fe–Zn, DMC catalysts were highly active even for the simultaneous transesterification of triglycerides and esterification of the free fatty acids (FFA) present in unrefined and waste cooking oils as well as non-edible oils. The transesterification of soybean oil with methanol to methyl esters was carried out using NaX zeolites loaded with KOH as a solid base catalyst by Wenlei Xie et al. [8]. Best result was obtained with NaX zeolite loaded with 10% KOH, followed by heating at 393 K for 3 h. Chawalit Ngamcharussrivichai et al. [9] studied the heterogeneously catalyzed transesterification of palm kernel oil with methanol over various modified dolomites at 60 °C. The modification of dolomite was performed via a conventional precipitation method using various nitrate salt solutions of alkali earth metals and trivalent metals. Influences of a variety of metals, calcination temperature of the parent dolomite, methanol/oil molar ratios, reaction time, catalyst amount, and catalyst reuse were investigated. The results indicated that the calcination temperature of the parent dolomite was a crucial factor affecting the activity and the basicity of the resulting catalyst. J. Ni and F.C. Meunier [10] studied the esterification of free fatty acids (FFA) found in vegetable oils with CH_3OH using a solid catalyst to convert FFA into valuable fatty acid methyl ester (FAME, biodiesel) and obtain a FFA-free oil that could be further transesterified using alkali bases. The authors also determined the active and durable solid catalysts for the esterification of palmitic acid (PA, $C_{16}H_{32}O_2$) dissolved in commercial sunflower oil with methanol.

A K/γ-Al_2O_3 catalyst was prepared by D. Martín Alonso et al. [11] using the wet impregnation method with K_2CO_3 as a precursor salt. During the activation process, a clear interaction between potassium carbonate-derived species and the support took place resulting in the formation of K aluminate-like species, as observed by evolved gas analysis by mass spectrometry (EGA-MS) and infrared spectroscopy (FTIR). This catalyst was tested in the transesterification of sunflower oil with methanol, achieving a methyl ester yield close to 100% after 1 h. However, when it was used in successive runs the catalyst showed a strong decrease in its catalytic performance. The present work stresses the obligation of the reutilization and of the verification of the leaching of active species in analogous catalytic systems based on alkaline and alkaline-earth metal oxides when used in the transesterification reaction with methanol. A new group of basic catalysts supported on mesoporous solids was prepared by Mônica C.G. et al. [12] and used as heterogeneous catalysis in biodiesel production. These catalysts based on calcium oxide supported on porous silica (SBA-15, MCM-41 and fumed silica) were characterized and evaluated in transesterification processes. The catalytic activity was evaluated in the transesterification of ethyl butyrate with methanol, and different reaction parameters were optimized by a factorial design response surface methodology. The transesterification activity of vegetable oils confirmed the results obtained in the reaction of ethyl butyrate with methanol, reaching conversion as high as 95% with sunflower oil (after 5 h of reaction) and 65% (after 1 h) for castor oil. The active phase of calcium oxide was investigated by characterizing the catalyst collected after achieving the conversion of edible soybean oil into its methyl ester at reflux of methanol in a glass batch reactor by Masato Kouzu et al. [13]. The catalytic activity and selectivity of several compounds of the alkaline and alkaline-earth metals in the transesterification with methanol at 323 K of refined sunflower oil were evaluated by G. Arzamendi et al. [14]. Catalytic runs were conducted with a molar methanol/oil ratio of 12:1 in a batch reactor. The considered catalysts were Li, Na, K, Rb, Cs and Ca hydroxides, Na, K, Ca and Mg carbonates, Na and K bicarbonates, sodium phosphates as well as Ca and Mg oxides. Catalysts behaviour mainly depended on their homogeneous or heterogeneous character; that is, on their solubility in methanol. The chemical stability under reaction conditions of the most active heterogeneous catalysts was investigated by checking the presence of the metals in the reaction mixture.

Transesterification of palm kernel oil with methanol over mixed oxides of Ca and Zn was investigated batch wise at 60 °C and 1 atm by Chawalit Ngamcharussrivichai et al. [15]. CaO·ZnO catalysts were prepared via a conventional co-precipitation of the corresponding mixed metal nitrate solution in the presence of a soluble carbonate salt at near neutral conditions. Under the suitable transesterification conditions at 60 °C (catalyst amount = 10 wt.%, methanol/oil molar ratio = 30, reaction time = 1 h), the ME content of >94% could be achieved over CaO·ZnO catalyst with the Ca/Zn ratio of 0.25. The mixed oxide could be also applied to transesterification of palm olein, soybean, and sunflower oils. Furthermore, the effects of different regeneration methods on the reusability of

CaO·ZnO catalyst were investigated. A new heterogeneous catalyst for the esterification of free fatty acids and the transesterification of vegetable oils was reported by Claudiney Soares Cordeiro [16]. The layered compound zinc hydroxide nitrate ($Zn_5(OH)_8(NO_3)_2·2H_2O$) was very effective in the alcoholysis of palm oil and the esterification of lauric acid with m(ethanol), even when hydrated ethanol was used. The catalytic properties of calcined Li–Al, Mg–Al and Mg–Fe layered double hydroxides (LDHs) were examined in two transesterification reactions, namely, the reaction of glyceryl tributyrate with methanol and the reaction of soybean oil with methanol by J. Link Shumaker [17]. While the Li–Al catalysts showed high activity in these reactions at the reflux temperature of methanol, the Mg–Fe and Mg–Al catalysts exhibited much lower methyl ester yields. The use of a heterogeneous catalyst, in the transesterification reaction of refined and acidic cottonseed oil for the production of methyl-esters (biodiesel) was studied by N. Barakos et al. [18]. The basic Mg–Al–CO_3 hydrotalcite catalyst used showed a high activity for methanolysis and esterification reactions in a refined and an acidic cottonseed oil as well as in a representative high water content animal fat feed. The experiments were performed in a temperature range between 180 and 210 °C, in a batch reactor. The methanol to vegetable oil molar ratio was 6 to 1, while the catalyst concentration was fixed at 1 wt.% of the oil mass. Non-calcined and calcined forms of the catalyst were tested. They found that the activity of the calcined catalyst was lower than the initial activity of the non-calcined catalytic system but it appeared the same with the reused non-calcined system. Catalytic reactivity was investigated by using methanolysis of soybean oil as probe reaction by Yanchang Wang et al. [19]. The MgO·$MgAl_2O_4$ composite showed a higher biodiesel yield compared to an MgO/$MgAl_2O_4$/γ-Al_2O_3 material with the same loading of magnesium prepared by a conventional impregnation method. The enhanced catalytic activity of the former material could be ascribed to its higher basicity, specific surface area, pore volume and pore size.

J.M. Marchetti and A.F. Errazu [20] found that ethanol and sulfuric acid were suitable to perform not only the transesterification reaction but also the direct esterification reaction to increase biodiesel production of the process. Hong-yan Zeng et al. [21] found that the hydrotalcite catalyst calcined at 773 K with Mg/Al molar ratio of 3.0 exhibited the highest catalytic activity in the transesterification. In addition, a study for optimizing the transesterification reaction conditions such as molar ratio of the methanol to oil, the reaction temperature, the reaction time, the stirring speed and the amount of catalyst, was performed. The removal of free fatty acid (FFA) in waste frying oil by esterification with methanol was conducted using various zeolite catalysts by Kyong-Hwan Chung et al. [22]. The effects of acidic properties and pore structure of the zeolite catalysts were discussed relating to the conversion of the FFA.

Different catalysts, such as solid resins, zeolite and enzymes, as well as different alcohols: ethanol anhydrous, ethanol 96°, 1-propanol, 2-propanol and butanol, were tested for the direct esterification reaction of pure oleic acid by J.M. Marchetti and A.F. Errazu [23]. The catalytic activity of a series of Mg–Zr catalysts with varying Mg to Zr ratios was evaluated for the room temperature transesterification of both edible and non-edible oils to their corresponding fatty acid methyl esters by Rekha Sree et al. [24]. The catalyst with Mg/Zr (2:1 wt./wt.%) exhibited exceptional activity towards transesterification reaction within short reaction time. The effects of different reaction parameters such as catalyst to oil mass ratio, reaction temperature, reaction time and methanol to oil molar ratio were studied to optimize the reaction conditions. The reasons for the observed activity of these catalysts were discussed in terms of their basicity and other physico-chemical properties.

The transesterification reaction was carried out with methanol and by using sulfuric acid and a Dowex DR2030 sulfonic resin as homogeneous and heterogeneous catalysts, respectively by D. Martín Alonso et al. [25]. A very positive effect was found in heterogeneous acid catalysis if H-bonds could stabilize the active intermediate participating in the rate determining step. The esterification of free fatty acids (FFA) in waste cooking oil with methanol in the presence of $Fe_2(SO_4)_3$/C (ferric sulfate/active carbon) catalyst was studied by Mengyu Gan et al. [26]. The effects of different temperatures, methanol/FFA mole ratio and amount of catalyst on the conversion of FFA were investigated. A single-step method was developed for biodiesel production from unrefined or waste oils using a series of heterogeneous zinc and lanthanum mixed oxides by Shuli Yan et al. [27]. A strong interaction between Zn and La species was observed with enhanced catalyst activities. Lanthanum promoted zinc oxide distribution and increased the surface acid and base sites. Transesterification of soybean oil catalyzed by combusted oyster shell, which is waste material from shellfish farms, was examined by Nobutake Nakatani et al. [28]. Powdered oyster shell combusted at a temperature above 700 °C, at which point the calcium carbonate of oyster shell transformed to calcium oxide, acted as a catalyst in the transesterification of soybean oil. On the basis of factorial design, the reaction conditions of catalyst concentration and reaction time were optimized in terms of the fatty acid methyl ester concentration expressed as biodiesel purity. Under the optimized reaction conditions of a catalyst concentration and reaction time of 25 wt.% and 5 h, respectively, the biodiesel yield, expressed relative to the amount of soybean oil poured into the reaction vial, was more than 70% with high biodiesel purity. Thiam Leng Chew and Subhash Bhatia [29] studied the catalytic cracking of crude palm oil (CPO) and used palm oil (UPO) in a transport riser reactor for the production of biofuels at a reaction temperature of 450 °C, with residence time of 20 s and catalyst-to-oil ratio (CTO) of 5 g g^{-1}. The effect of HZSM-5 (different Si/Al ratios), beta zeolite, SBA-15 and AlSBA-15 was studied as physically mixed additives with cracking catalyst.

The catalytic activity of zeolites was studied in the esterification of oleic acid with methanol in soybean oil by Kyong-Hwan Chung and Byung-Geon Park [30]. The influences of acidity and pore structure of the zeolites were investigated in relation to conversion of the oleic acid on the zeolite catalysts. Yee Kang Ong and Subhash Bhatia [31] investigated the composite catalyst containing H-Y zeolite and kaolin suitable for catalytic cracking of palm oil for the production of biofuels. The authors reported the results of the hydrodynamic studies using a composite catalyst in a transport riser reactor. A series of catalysts containing 5–30 wt% of 12-tungstophosphoric acid (TPA) supported on niobia was prepared and its catalytic activity was evaluated for the esterification of free fatty acids with methanol by K. Srilatha et al. [32]. They observed that esterification activity depended upon the structural variations of the catalyst. The effects of reaction variables such as catalyst loading, methanol to acid ratio, reaction time and temperature on the conversion of fatty acid were studied. The esterification activity of the catalysts was correlated with the characteristics of the catalysts. M.S. Kotwal et al. [33] used flyash-based base catalyst in the transesterification of sunflower oil with methanol to methyl esters in a heterogeneous manner. Catalyst preparation variables such as the KNO_3 loading amount and calcination temperature were optimized. The catalysts were characterized by powder XRD. The catalyst was prepared by loading 5 wt.% KNO_3 on flyash followed by its calcination at 773 K exhibited maximum oil conversion (87.5 wt.%). The influence of various reaction parameters such as % catalyst loading, methanol to oil molar ratio, reaction time, temperature, reusability of the catalyst on the catalytic activity was investigated.

The response surface methodology (RSM) in conjunction with the central composite design (CCD) was used to optimize the activity of CaO/Al_2O_3 solid catalysts for the production of biodiesel by Masoud Zabeti et al. [34]. In order to measure the catalyst activity,

the authors used palm oil as a representative raw material for the conversion to biodiesel. The biodiesel production was carried out in a batch laboratory scale reactor. The results showed that both the calcination temperature and the amount of calcium oxide loaded on the support had significant positive effects on the biodiesel yield. The dissolution of calcium oxide catalysts in products and their repeated uses were also investigated to discuss their advantages as heterogeneous catalysts in the production of biodiesel by Yung Bok Cho et al. [35]. Man Kee Lam et al. [36] studied the effect of super acid sulfated tin oxide catalyst on tranesterification process. Young-Moo Park et al. [37] examined tungsten oxide zirconia, sulfated zirconia and Amberlyst-15 as a catalyst for a conversion of used vegetable oils (VOs) to fatty acid methyl esters (FAMEs). They found that the tungsten oxide zirconia was a promising heterogeneous catalyst for the production of biodiesel fuels from used VOs because of high activity in the conversion over 93% and the absence of leaching WO_3 in the esterification reaction. Ji-Yeon Park et al. [38] compared the two kinds of heterogeneous acid catalysts, Amberlyst 15 and Amberlyst BD20, to produce biodiesel from high free fatty acid (FFA) oils, the esterification characteristics.

Sinem Çaynak et al. [39] reported that the maximum yield of methyl ester from pomace oil was obtained at 30% of methanol/oil ratio, 60 °C temperature for 60 min with NaOH catalyst. Essam Al-Zaini et al. [40] studied the production of biodiesel fuel from waste cooking oil with ethanol in the presence of tri-potassium phosphate (K_3PO_4) as a solid base heterogeneous catalyst. The principal variables for the present study were, ethanol/oil molar ratio (6:1 to 12:1), catalyst concentration (2–8 wt%), stirring speed (600–1800 rpm), reaction temperature (30–70 °C) and time (1–3 h). The transesterification of soybean oil with a CaO/mesoporous silica catalyst was carried out by Chanatip Samart et al. [41]. The effects of CaO loading levels in the mesoporous silica catalyst, the amount of catalyst to substrate level and reaction temperature and time on the conversion of soybean oil were investigated. Increasing the temperature and time raised the total conversion of soybean oil attained. Biodiesel had been produced by transesterification of canola oil with methanol in the presence of highly Brønsted acidic ionic liquids based on 1-benzyl-1*H*-benzimidazole, and the effect of reaction temperature, type and amount of catalyst, molar ratio and reaction time was investigated M. Ghiaci et al. [42]. The results showed that the 4B ionic liquid had the highest catalytic activity and best recyclability under the optimised reaction conditions. Thus, this ionic liquid was able to catalyze the transesterification of canola oil to its methyl esters in 5 h with yields of more than 95%. Density functional calculations (B3LYP), using the 6-311G basis set, had been performed to have a better understanding of the reactivity of these catalysts. The catalytic activity of 4B for the transesterification of other vegetable oils and alcohols was also studied.

3. Effect of catalyst on biodiesel performance characteristics

Researchers and scientists had studied the performance characteristics of diesel engine when a catalyst/additive was used along with biodiesel. Most of the researchers/scientists reported that the effect of the catalyst on the performance of diesel engine fuelled with biodiesel was not much significant.

Ali Keskin et al. [43] investigated the influences of Mg and Mo based fuel additives on diesel engine performance running with tall oil biodiesel. A single cylinder DI diesel engine was used in the tests. The authors found that the engine performance values did not change significantly with biodiesel fuels. Metin Gürü studied et al. [44] the chicken fat biodiesel with synthetic Mg additive was studied in a single-cylinder, direct injection (DI) diesel engine and its effects on engine performance and exhaust emissions were studied. Organic based synthetic magnesium additive was doped into the biodiesel blend by 12 μmol Mg. Engine tests were run with diesel fuel (EN 590) and a blend of 10% chicken fat biodiesel and diesel fuel (B10) at full load operating conditions and different engine speeds from 1800 to 3000 rpm. The results showed that, the engine torque was not changed significantly with the addition of 10% chicken fat biodiesel, while the specific fuel consumption increased by 5.2% due to the lower heating value of biodiesel. A.S. Ramadhas et al. [45] experimentally proved that the diethyl ether could be used as an additive with biodiesel to improve the performance characteristics. An experimental investigation was conducted by Theodore Constantine Zannis et al. [46] to determine the effect of oxygen content and oxygenate type on DI diesel engine performance and emissions. One conventional and three oxygenated fuels were examined having an oxygen content ranging from 0% to 9%. The fuels were prepared by blending a biodiesel compound (RME), diglyme and butyl-diglyme with a low-sulfur diesel fuel in various proportions. An experimental installation was prepared and engine tests were conducted on a naturally aspirated single-cylinder Ricardo Hydra research engine. The measurements were carried out at various operating conditions. In addition, a slight increase of BSFC was observed due to the small decrease of fuel heating value with the increase of the oxygen content. Similar effects were observed when replacing the rapeseed methyl ester with a mixture of diglyme and butyl-diglyme and the oxygen percentage remained unaltered.

Ali Keskin et al. [47] studied the effect of metallic fuel additive on performance characteristics of diesel engine fuelled with tall oil methyl ester. Metallic fuel additives improved properties of biodiesel fuels, such as pour point and viscosity values. Biodiesel fuels were tested in an unmodified direct injection diesel engine at full load condition. Specific fuel consumption of biodiesel fuels increased by 6.00%, however, in comparison with TE60 (Tall oil methyl ester), it showed a decreasing trend with use of additives. G.R. Kannan et al. [48] investigated the use of ferric chloride ($FeCl_3$) as a fuel borne catalyst (FBC) for waste cooking palm oil based biodiesel. The metal based additive was added to biodiesel at a dosage of 20 μmol/L. Experiments were conducted to study the effect of ferric chloride added to biodiesel on performance of a direct injection diesel engine operated at a constant speed of 1500 rpm at different operating conditions. The results revealed that the FBC added biodiesel resulted in a decreased brake specific fuel consumption (BSFC) of 8.6% while the brake thermal efficiency increased by 6.3%.

4. Effect of catalyst on biodiesel combustion characteristics

Researchers and scientists' studied combustion characteristics of diesel engine when catalyst/additive was used along with biodiesel.

The influence of ferrocene as a fuel additive on heat release rates was studied by C.J. Du et al. [49] in single cylinder diesel engine. Two engine configurations were tested: standard aluminum piston with normal engine deposits and a second test with the engine cleaned to "new engine condition", but with the piston replaced with a thermal barrier coated piston. Heat release rates and IMEPs were calculated from in-cylinder pressure data. Nanoparticle concentrations (diameter < 50 nm) appeared to be sensitive to small changes in heat release rates, so these particulate trends suggested surface conditioning that produced changes in heat release patterns. Heat release profiles showed an intriguing shift during one 175 min period of stable aluminum piston operation. The 30 and 40% burn angles advanced while 5 and 60% burn angles remained unchanged. Eiji Kinoshita et al. [50] experimentally found that the ignition delay of biodiesel became longer by adding crude glycerine to biodiesel.

The potential of diethyl ether (DEE) which is a renewable bio-based fuel was identified as a supplementary oxygenated additive to improve fuel properties and combustion characteristics of biodiesel (Karanja oil methyl ester – KOME) like its high viscosity, cold starting problems through an experimental investigation by Masoud Iranmanesh [51]. The tests were conducted on a single-cylinder DI diesel engine fuelled with neat KOME as a base fuel and blends of 5, 10, 15 and 20% DEE on a volume basis. Some physicochemical properties of test fuels such as heating value, viscosity, specific gravity and distillation profile were determined in accordance to the ASTM standards. Hu Li et al. [52] investigated the effect of a multifunctional diesel fuel additive package used with rapeseed oil (RSO) as a fuel in a DI heavy-duty diesel engine. The aim was to maintain combustion performance and prevent the deterioration of exhaust emissions associated with injector deposit build up. Two scenarios were investigated: the effect of deposit clean-up by a high dose of the additive package and the effect of deposit prevention using a moderate dose of the additive package. Engine combustion performance was compared for each case against the use of RSO without any additive. The results showed that the use of the multifunctional fuel additive package reduced the ignition delay (ID), increased the premixed combustion duration (PCD) and improved the combustion stability. The multifunctional fuel additive package also reduced the deposit build up on the fuel injectors and prevented the deterioration of engine. An experimental investigation was conducted by D.H. Qi et al. [53] to evaluate the effects of using diethyl ether and ethanol as additives to biodiesel/diesel blends on the combustion characteristics of a direct injection diesel engine. The test fuels were denoted as B30 (30% biodiesel and 70% diesel in vol.), BE-1 (5% diethyl ether, 25% biodiesel and 70% diesel in vol.) and BE-2 (5% ethanol, 25% biodiesel and 70% diesel in vol.), respectively. The peak pressure rise rate and peak heat release rate of BE-1 were almost similar to those of B30, and higher than those of BE-2 at lower engine loads. At higher engine loads the peak pressure, peak pressure rise rate and peak heat release rate of BE-1 were the highest and those of B30 were the lowest. BE-1 reflects better combustion characteristics than BE-2 and B30.

5. Effect of catalyst on biodiesel emission characteristics

Researchers and scientists studied the effect of catalyst on emission characteristics. A brief review of their findings is presented here.

Robert L. McCormick et al. [54] studied the effect of fuel additive and blending approaches to reducing NO_x emissions from biodiesel. Polyisobutylene (PIB), a high molecular weight polymer fuel additive, was extensively tested in heavy-duty diesel engines to determine its effect on both controlled and presently un-controlled exhaust emissions by Donel R. Olson et al. [55]. Idle particulate matter emissions were reduced on the order of 60%. Simultaneously, 1,3-butadiene, a high risk carcinogenic compound in diesel engine exhaust was essentially eliminated with the PIB additive-treated fuel and all polycyclic aromatic hydrocarbons were reduced compared to the baseline exhaust emission data without PIB. These results and emission reductions were all obtained with a 5 ppm concentration of the PIB additive in CARB-specification-diesel and biodiesel fuels. Kalam M.A. and Masjuki H.H. [56] presented the experimental test results of a diesel engine using additive-added palm biodiesel (it is also known as palm diesel) obtained from palm oil. The emission test was done with a dynamometer fixed load of 50 Nm and constant engine speed of 2250 rpm. A total of three fuels, such as 100% diesel fuel (B0); 20% palm diesel and 80% B0 (B20); and B20 with *X*% additive (B20*X*), were selected for this investigation. It was found that B20*X* fuel showed better overall performance such as improved brake power, reduced exhaust emissions and better lube oil quality as compared to other tested fuels. This was mainly due to the effect of fuel additive in the blended fuel of B20. The specific objective of this investigation was to develop the performance of B20 fuel by using an in-house-formulated fuel additive. Detailed results were presented with discussions. In this study, the efforts to reduce NO_x and particulate matter (PM) emissions from a diesel engine using both ethanol-selective catalytic reduction (SCR) of NO_x over an Ag/Al_2O_3 catalyst and a biodiesel-ethanol–diesel fuel blend (BE-diesel) on an engine bench test were discussed by Xiaoyan SHI et al. [57]. The engine bench test results indicated that the combination of BE-diesel and a SCR catalyst assembly could provide benefits for NO_x and PM emission control even without using diesel particle filters (DPFs). Fujia Wu [58] studied the effect of different biodiesel and their blends with oxygenated additives on emissions from diesel engine. Performance and emission studies of diesel engine using diethyl ether as oxygenated fuel additive were conducted by Kapilan Natesan [59]. A prototype catalyst was developed and integrated within the aftertreatment exhaust system to control the HC, CO, PM and NO_x emissions from diesel exhaust gas by Kampanart Theinnoi et al. [60]. The catalyst activity in removing HC and nanoparticles was examined with exhaust gas from a diesel engine operating on biodiesel — rapeseed methyl ester (RME). The tests were carried out at steady-state conditions for short periods of time, thus catalyst tolerance to sulfur was not examined. The prototype catalyst reduced the amount of hydrocarbons (HC) and the total PM. Moreover, it was observed that the use of EGR (20 vol.%) for the biodiesel-fuelled engine significantly increased the particle concentration in the accumulation mode with simultaneous reduction in the particle concentration in the nuclei mode. The effectiveness of the prototype catalyst in reducing PM from the combustion of biodiesel was dependent on the engine operating condition and EGR. The results suggested that the use of this prototype catalyst could aid aftertreatment system performance and the control of environmental pollution.

Z.H. Zhang et al. [61] aimed to investigate the combined application of fumigation methanol and a diesel oxidation catalyst for reducing emissions of an in-use diesel engine. Experiments were performed on a 4-cylinder naturally aspirated direct-injection diesel engine operating at a constant speed of 1800 rpm for five engine loads. The fumigation method resulted in a significant increase in hydrocarbon (HC), carbon monoxide (CO), and nitrogen dioxide (NO_2) emissions, but a decrease in nitrogen oxides (NO_x), smoke opacity and the particulate mass concentration. For the submicron particles, the total number of particles decreased. In all cases, there was little change in geometrical mean diameter of the particles. After catalytic conversion, the HC, CO, NO_2, particulate mass and particulate number concentrations were significantly reduced at medium to high engine loads; while the geometrical mean diameter of the particles became larger. Thus, the combined use of fumigation methanol and diesel oxidation catalyst led to a reduction of HC, CO, NO_x, particulate mass and particulate number concentrations at medium to high engine loads. Chinnathambi Swaminathan [62] studied the effect of additives diethylene glycol mono methyl ether and diethylene glycol monobutyl ether on NO_x emission.Kang-Shin Chen et al. [63] demonstrated that the emulsified bio-solution/palm-biodiesel/diesel blends had the advantage in saving energy and reducing emissions of both polycyclic aromatic hydrocarbons (PAHs) and particulate matter (PM) from diesel engines. When compared with P0 (premium diesel fuel as base fuel), E16P20 fuel (16 vol.% bio-solution + 20 vol.% palm-biodiesel + 64 vol.% P0, an additional 1 vol.% surfactant) saved 12.4% fuel consumption and reduced emissions of PM by 90.1%, total PAHs by 69.3%, and total BaP_{eq} (benzo[a]pyrene equivalent concentration) by 69.6%. Emulsified palm-biodiesel with bio-solution can be considered as a clean and alternative fuel. Grisel Corro et al. [64] investigated the activity of pre-sulfated 1%Pt–2%Sn/γ-Al_2O_3 on the

catalytic abatement of the combustion emissions of three fuels: pure diesel $E(0)$, pure bioethanol $E(100)$ and bioethanol blended diesel containing 10% bioethanol $E(10)$. The emissions generated, by each blend were conducted continuously to the catalyst sample. The catalytic activity was determined by following the evolution of the outflow emission concentrations by FTIR gas spectroscopy as a function of the catalyst temperature. Results showed that the addition of bioethanol to diesel might be necessary to enhance the catalytic oxidation of diesel unburned hydrocarbons and particulate matter on pre-sulfated 1%Pt–2%Sn/γ-Al_2O_3. Donghui Qi et al. [65] studied the effect of injection timing and EGR rate on the emissions of a Ford Lion V6 split injection strategy direct injection diesel engine using neat biodiesel produced from soybean oil. The authors mainly focused their attention on the determination of the main injection timing and EGR rate for biodiesel with the aim to reduce all engine harmful emissions, especially NO_x and soot. K. Varatharajan et al. [66] studied the effect of antioxidant additives on NO_x emissions in a jatropha methyl ester fuelled direct injection diesel engine have been investigated experimentally and compared.

6. Conclusions

The literature related to the effect of catalyst/additive on biodiesel combustion and performance has been found to be limited. Biodiesel production was improved by 98% with the use of catalyst. The calcined hydrotalcite with an Mg/Al ratio of 3.0 derived from calcination at 773 K was found to be the optimum catalyst that could give the highest basicity and the best catalytic activity for this reaction. The effectiveness of the prototype catalyst in reducing PM from the combustion of biodiesel was dependent on the engine operating condition and EGR. The results suggested that the use of this prototype catalyst could aid aftertreatment system performance and the control of environmental pollution. The results showed that the use of the multifunctional fuel additive package reduced the ignition delay (ID), increased the premixed combustion duration (PCD) and improved the combustion stability. The multifunctional fuel additive package also reduced the deposit build up on the fuel injectors and prevented the deterioration of engine with the addition of 10% chicken fat biodiesel, while the specific fuel consumption increased by 5.2% due to the lower heating value of biodiesel. The effectiveness of the prototype catalyst in reducing PM from the combustion of biodiesel was dependent on the engine operating condition and EGR. The results suggested that the use of this prototype catalyst could aid aftertreatment system performance and the control of environmental pollution.

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